

**Title:** **THERMAL PASTE FOR  
IMPROVING THERMAL  
CONTACTS**

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## THERMAL PASTE FOR IMPROVING THERMAL CONTACTS

[0001] This application claims the benefit of United States Provisional Patent Application Serial No. 60/485,804, filed July 9, 2003, which is hereby incorporated by reference in its entirety.

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### **FIELD OF THE INVENTION**

[0002] This invention relates to a thermally conductive paste for improving thermal contacts.

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### **BACKGROUND OF THE INVENTION**

[0003] With the miniaturization and increasing power of microelectronics, heat dissipation has become critical to the performance, reliability and further miniaturization of microelectronics. Heat dissipation from microelectronics is most commonly performed by thermal conduction. For this purpose, a heat sink, which is a material of high thermal conductivity, is commonly used. In order for the heat sink to be well utilized, the thermal contact between the heat sink and the heat source (e.g., a substrate with a semiconductor chip on it) should be good. Wolff et al., *Heat & Mass Transfer* 41:3469-3482 (1998); Ouellette et al., *Proc. Power Elec. Des. Con., Power Sources Users Conf., Cerritos, CA*, pages 134-138 (1985).

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[0004] A thermal fluid or paste is commonly applied at the interface to enhance the thermal contact. Vogel, *Proc. Int. Intersoc. Elec. Pkg. Conf., Adv. in Elec. Pkg., Am. Soc. Mech. Eng., NY, NY* 10-2:989 (1995). The fluid or paste is a material that has high conformability so that it can conform to the surface topography of the mating surfaces, thereby avoiding air gaps (which are thermally insulating) at the interface. The fluid or paste must be highly spreadable, so that the thickness of the paste after application is very thin (just enough to fill the valleys in the surface topography of the mating surfaces). Preferably the fluid or paste is thermally conductive as well. Although much attention has been given to the development of heat sink materials, relatively little attention has been given to the development of thermal fluids or pastes.

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[0005] The most common thermal fluid is mineral oil. As a fluid, it is highly conformable and spreadable, but it has a low thermal conductivity. The most common thermal paste is silicone filled with thermally conductive particles. Wilson et al., *Nat. Elec. Pkg. & Prod. Conf., Proc. Tech. Prog., Reed Exh. Co., Norwalk, CT* 2:788-796 (1996); Peterson, *Proc. 40th Elec. Comp. & Tech. Conf., IEEE, Piscataway, NJ* 1:613-619 (1990); Lu et al., *J. Polym. Sci., Part B* 36:2259-2265 (1998); Sasaski et al., *Jap. IEMT Symp. Proc., IEEE/CPMT Int. Elec. Mfg. Tech. Symp., IEEE, Piscataway, NJ* 236-239(1995). Due to the filler, it is relatively high in thermal conductivity, but it suffers from poor conformability and poor spreadability. Thermal fluids and pastes of previous work are not as effective as solder (applied when it is molten), but they do not require heating, which is required for the use of solder. Xu et al., *J. Electron. Pkg.* 124:188-191 (2002); Xu et al., *J. Electron. Pkg.* 122:128-131 (2000).

[0006] Due to its excellent heat transfer characteristics and as it is relatively inexpensive, boron nitride is commonly used as a filler for thermal interface materials. Unfortunately, however, it suffers from the disadvantage that it degrades when exposed to humidity. When placed in a humid environment, hygroscopic impurities (boric oxide) within the compound absorb atmospheric water, which then reacts with the boron nitride to form boric acid. Being hygroscopic, the boric acid absorbs further water, thereby accelerating the degradation of the boron nitride and diminishing its heat removing capabilities, which ultimately leads to failure of the device. Published PCT Application WO 01/21393 is specifically directed to this problem and describes a moisture resistant, thermally conductive material that includes thermally conductive filler particles, preferably boron nitride, that are coated with a hydrophobic compound, preferably a silicone compound such as a siloxane. The hydrophobic compound-coated filler particles are joined together with a binder, and account for between 5 and 70 vol.% of the material.

[0007] Organic vehicles are commonly used as the suspending medium for dispersed inorganic particles in pastes. Kumar, *Active & Passive Elec. Comp.* 25:169-179(2002); Chae et al., *Mater. Lett.* 55:211-216 (2002); Heller et al., *Tenside, Surfactants, Detergents* 29:315-319 (1992); Stanton, *Int. J. Hybrid.*

*Microelec.* 6:419-432 (1983). An organic vehicle system may consist of a solvent (such as butyl ether) (Bernazzani et al., *J. Chem. Therm.* 33:629-641 (2001)) and a solute (such as ethyl cellulose) (Stanton, *Int. J. Hybrid Microelec.* 6:419-432 (1983)), which serves to enhance the dispersion and suspension. Kumar, *Active & Passive Elec. Comp.* 25:169-179(2002). Ethyl cellulose has the further advantage of its slight conductivity. Khare et al., *Polym. Int.* 42:138-142 (1997); Khare et al., *Polym. Int.* 49:719-727 (2000).

[0008] Another organic vehicle is polyethylene glycol (PEG), a polymer of low molecular weight (400 amu), which is different from silicone in its low viscosity. By using PEG in conjunction with boron nitride particles as a thermal paste between copper disks, a thermal contact conductance of  $1.9 \times 10^5 \text{ W/m}^2\cdot^\circ\text{C}$  has been attained. This value is higher than that obtained by using a thermal paste involving silicone and boron nitride powder ( $1.1 \times 10^5 \text{ W/m}^2\cdot^\circ\text{C}$ ), but is lower than that obtained by using solder, applied in the molten state ( $2.1 \times 10^5 \text{ W/m}^2\cdot^\circ\text{C}$ ). Xu et al., *J. Electron. Pkg.* 124:188-191 (2002). In fact, all thermal pastes previously reported are inferior to solder in providing high thermal contact conductance.

[0009] Carbon black is a very fine particulate form of elemental carbon, consisting of typically spherical particles, which in turn come together to form porous agglomerates. Carbon black is produced either by incomplete combustion or thermal decomposition of a hydrocarbon feedstock. Types of carbon black include soot, lamp black (typical particle size 50-100 nm), channel black (typical particle size 10-30 nm), furnace black (typical particle size 10-80 nm), thermal black (typical particle size 150-500 nm), and acetylene black (typical particle size 35-70 nm).

[0010] Carbon black is used as a low-cost electrically conductive filler in polymers. Nakamura et al., *NEC Res. & Dev.* 83:121-127 (1986); Saad et al., *J. Appl. Polym. Sci.* 73:2657:2670 (1999). Due to its relatively low thermal conductivity, however, carbon black has not been reported as a filler for thermally conductive pastes. Most commonly, it is used as a reinforcement in rubber. Takirio et al., *Tire Sci. & Tech.* 26:241-257 (1998); Haws et al., *Rub. Div. Symp., ACS, Akron, OH* 1:257-281 (1982); Hess et al., *Rub. Chem. & Tech.* 56:390-417

(1983); Kundu et al., *J. Appl. Polym. Sci.* 84:256-260 (2002); Ramesan et al., *Plas. Rub. & Comp.* 30:355-362 (2001); Sridhar et al., *J. Appl. Polym. Sci.* 82:997-1005 (2001).

[0011] In addition, carbon black is used in electrochemical electrodes  
5 (Takei et al., *J. Power Sources* 55:191-195 (1995); Van Deraerschot et al.,  
*Electrochem. Soc. Ext. Abst., Electrochem. Soc., Pennington, NJ* 84:139 (1984)),  
inks (Erhan et al., *J. Am. Oil Chem. Soc.* 68:635-638 (1991); Bratkowska et al.,  
*Przemysl Chemiczny* 66:393-395 (1987); Bratkowska et al., *Przemysl Chemiczny*  
65:363-365(1986)), lubricants (Chinas-Castillo et al., *Tribology Trans.* 43:387-  
10 394 (2000); Shiao et al., *J. Appl. Polym. Sci.* 80:1514-1519 (2001); Kozlovtssev et  
al., *Glass & Ceramics (English Translation of Steklo I Keramika)* 154-157;  
Bakaleinikov et al., *Chem. & Tech. Fuels & Oils* 18:108-111 (1982)), fuels  
(Srivastava et al., *Fuel* 73:1911-1917 (1984); Steinberg, *Preprints: Div. Pet.*  
*Chem., ACS* 32:565-571 (1987); Smith, *Automotive Eng. (London)* 7:23-24, 27  
15 (1982)), and pigments (Ueki et al., *Ann. Conf. Elec. Ins. & Dielec. Phen., Ann.*  
*Rpt., IEEE, Piscataway, NJ* 1:170-176 (1997)).

[0012] The present invention is directed to overcoming these and other  
deficiencies in the art.

## 20 SUMMARY OF THE INVENTION

[0013] One aspect of the present invention relates to a thermally  
conductive paste formed from porous agglomerates of carbon particles dispersed  
in a paste-forming vehicle.

[0014] Another aspect of the present invention is directed to a thermally  
25 conductive interface material in the form of a paste formed from porous  
agglomerates of carbon particles dispersed in a paste-forming vehicle.

[0015] A further aspect of the present invention is an apparatus that  
includes a heat source, a heat sink proximate the heat source, and a layer of a  
thermally conductive paste made in accordance with the present invention  
30 disposed between and in contact with the heat source and the heat sink.

[0016] Yet another aspect of the present invention is a method of  
removing heat from a heat source that involves providing a heat sink proximate

the heat source and disposing a layer of a thermally conductive paste made in accordance with the present invention between and in contact with the heat source and the heat sink.

[0017] The thermally conductive paste of the present invention is highly conformable and spreadable and is particularly useful as a thermally conductive interface material. By using porous agglomerates of carbon particles as the thermally conductive ingredient, thermal pastes that are superior to solder in providing high thermal contact conductance have been attained. Thermally conductive interface materials prepared in accordance with the present invention can provide thermal contact conductance between copper disks of  $3 \times 10^5$  watts/meter<sup>2</sup>.°C ( $W/m^2 \cdot ^\circ C$ ), as compared to  $2 \times 10^5 W/m^2 \cdot ^\circ C$  for solder. Moreover, the pastes are easy to use and apply, unlike solder, which requires the application of heat during use.

[0018] Thermally conductive pastes of the present invention have many applications. Pastes prepared in accordance with the present invention may be used, for example, for microelectronic cooling, for heat pipes for tapping geothermal energy (Lockett, *H. & V. Eng.* 59:7-8; Lockett, *Proc. Eur. Cong.*, 1:285-289 (1984)) and for thermal fluid heaters for providing indirect process heat (Dawes et al., *Inst. Energy, London, UK Pap. KN/III/2* 1:8pp (1984)). Pastes prepared in accordance with the present invention may also be used, for example, for the cooling of machinery, boilers, cutting tools, oil drilling equipment components, spacecraft components and building components. Other applications may be in connection with foods, wound healing, therapeutics, etc.

[0019] Thermally conductive pastes of the present invention may also be used to improve the thermal contact between a cold source and an object proximate the cold source, for the purpose of cooling the object or other objects connected to the object. The pastes, may for example, be applied to improve the thermal contact between a fluid-cooled object (the cold source) and a cold plate or a cold finger, for the purpose of cooling an object connected to the cold plate or cold finger.

[0020] Another aspect of the present invention is therefore, an apparatus that includes a cold source, an object proximate the cold source, and a layer of a

thermally conductive paste made in accordance with the present invention disposed between and in contact with the cold source and the object.

[0021] Yet another aspect of the present invention is a method of improving the thermal contact between a first object and a second object proximate the first object, that involves disposing a layer of a thermally conductive paste made in accordance with the present invention between and in contact with the first object and the second object.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

10 [0022] Figure 1 is a partial, perspective view of a layer of a thermally conductive paste made in accordance with the present invention disposed between an integrated circuit chip and a heat sink.

[0023] Figure 2 is a schematic representation of thermal contact conductance measurement in accordance with the present invention.

15 [0024] Figure 3 is a graphic representation of thermogravimetric results obtained for (a) PEG by itself; and (b) PEG with 3 vol.% ethyl cellulose.

[0025] Figure 4 is a graphic representation of thermogravimetric results obtained for (a) butyl ether by itself; and (b) butyl ether with 40 vol.% ethyl cellulose.

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### **DETAILED DESCRIPTION OF THE INVENTION**

[0026] The present invention relates to a thermally conductive paste formed from porous agglomerates of carbon particles dispersed in a paste-forming vehicle. The paste is particularly useful as a thermally conductive interface material for improving thermal contacts, such as, for example, between a heat source and a heat sink or between a cold source and an object. Thus, the present invention further relates to a thermally conductive interface material in the form of a paste formed from porous agglomerates of carbon particles dispersed in a paste-forming vehicle.

30 [0027] The porous agglomerates of carbon particles will preferably be a carbon black. Types of carbon black include soot, lamp black (typical particle size 50-100 nm), channel black (typical particle size 10-30 nm), furnace black

(typical particle size 10-80 nm), thermal black (typical particle size 150-500 nm), and acetylene black (typical particle size 35-70 nm), for example.

[0028] In one aspect, the paste-forming vehicle may be a paste-forming vehicle system. Typically, a paste-forming vehicle system will include a paste-forming solvent and a solute. The system may, for example, be organic-based or inorganic based. Examples of solvents that may be used in a paste-forming vehicle system can include, but are not limited to, silicates (such as, for example, sodium silicate), glycol ethers (such as, for example, di(ethylene glycol) butyl ether ("BE")), methoxypolyethylene glycol ("MPEG"), ethylene glycol, propylene glycol, ethylene oxide, propylene oxide, polyethylene glycol ("PEG"), PEG modified with various types of functional groups (such as, for example, -H, -CH<sub>3</sub>, etc.) at the ends of the macromolecular chain, oil, water, alcohols (such as, for example, 2-ethylhexanol, 2-ethylhexoic acid, 2-methyl butanol, propanol, ethanol, diacetone alcohol, isobutanol, isopropanol, *n*-butanol, *n*-pentanol, *n*-propanol, etc.), diethyl sulfate, diisobutyl carbinol, diisobutyl ketone, hexylene glycol, isobutyl acetate, isophorone, isopropyl acetate, methyl isobutyl carbinol, ketone (such as, for example, methyl isobutyl ketone), *n*-butyl acetate, *n*-propyl acetate, primary amyl acetate mixed isomers, primary amyl alcohol mixed isomers, *n*-propyl propionate, *n*-butyl propionate, *n*-pentyl propionate, methylene chloride, perchloroethylene, trichloroethylene, xylene, acetone, ethyl acetate, and chemically related substances.

[0029] Examples of solvents that may be used in a paste-forming vehicle system can include, but are not limited to, cellulosic resin, thermoplastic resin, glycidyl methacrylate, hydroxy(meth)acrylate monomers, epsilon-caprolactone monomer, hydroxypropyl acrylate, hydroxyethyl acrylate, ethylene acrylic acid, divinylbenzene, styrene-butadiene latexes, acrylic latexes, vinyl acrylic latexes, styrene acrylic latexes, vinyl versatate latexes, vinyl chloride, vinylbenzyl chloride, chloromethylstyrene, vinyl acetate copolymers, epoxy resins, epoxy acrylate, aminoethylethanolamine, glycol ethers, propylene glycols, ethylene glycols, polyols (e.g., aliphatic polyester polyols), ethylene acrylic acid resins, methylcellulose, ethyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol, starch, and chemically related substances. The choice of solute will typically depend on



the choice of solvent. At least the last four solutes, for example, are soluble in water.

**[0030]** An organic-based paste-forming vehicle system may include, for example, a solvent such as polyethylene glycol or di(ethylene glycol) butyl ether,  
5 and a solute, such as, for example, ethyl cellulose.

**[0031]** In some instances, such as with water-based and alcohol-based pastes, the solvent evaporates, allowing the conductive units (i.e., carbon black agglomerates) to be in intimate contact after the paste has dried. In contrast, oil-based and some polymer-based pastes do not dry. Ether itself is volatile, but the  
10 dissolution of a solute such as ethyl cellulose in it results in a paste-forming vehicle that is not volatile, such that the resulting paste does not dry, as in the case of certain polymer-based pastes.

**[0032]** In one aspect, a thermally conductive paste prepared in accordance with the present invention may, for example, incorporate a paste-forming vehicle  
15 system including PEG as a solvent and ethyl cellulose as a solute. In this aspect, the amount of ethyl cellulose present in the paste will preferably be within the range of about 3 to about 5 volume percent (vol. %). More preferably, the amount of ethyl cellulose present in the paste will be about 3 vol.%. Furthermore, the amount of carbon particles dispersed in the paste will preferably be less than about  
20 2.0 vol.%, and more preferably, less than about 1.5 vol.%.

**[0033]** A particularly useful thermally conductive paste of the present invention includes porous agglomerates of carbon particles dispersed in a paste-forming vehicle system including ethyl cellulose in PEG, where the amount of carbon particles dispersed in the paste is about 1.25 vol.% and the amount of ethyl  
25 cellulose present in the paste is about 3 vol.%.

**[0034]** In another aspect, a thermally conductive paste prepared in accordance with the present invention may, for example, incorporate a paste-forming vehicle system including di(ethylene glycol) butyl ether as a solvent and ethyl cellulose as a solute. In this aspect, the amount of ethyl cellulose present in  
30 the paste will preferably be about 40 vol.%. In addition, the amount of carbon

particles dispersed in the paste will preferably be less than about 0.40 vol.%, and more preferably, about 0.20 vol.%.

[0035] Another particularly useful thermally conductive paste of the present invention includes porous agglomerates of carbon particles dispersed in a paste-forming vehicle system including ethyl cellulose in di(ethylene glycol) butyl ether, where the amount of carbon particles dispersed in the paste is about 0.20 vol.% and the amount of ethyl cellulose present in the paste is about 40 vol.%.

[0036] Due to its high conformability and spreadability, the thermally conductive paste of the present invention is especially useful as a thermally conductive interface material to assist in heat transfer between a heat source and a heat sink, for example, between an integrated circuit chip and a heat sink for dissipation of heat from an electronic apparatus.

[0037] Particularly useful as a thermally conductive interface material is a paste of the present invention where the paste-forming vehicle is a paste-forming vehicle system including ethyl cellulose in PEG and the amount of carbon particles dispersed in the paste is about 1.25 vol.% and the amount of ethyl cellulose present in the paste is about 3 vol.%.

[0038] Also useful as a thermally conductive interface material is a paste of the present invention where the paste-forming vehicle is a paste-forming vehicle system including ethyl cellulose in di(ethylene glycol) butyl ether, where the amount of carbon particles dispersed in the paste is about 0.20 vol.% and the amount of ethyl cellulose present in the paste is about 40 vol.%.

[0039] Referring now to Figure 1, an electronic apparatus 10 made in accordance with the present invention includes a heat source 12, such as, an integrated circuit chip, and a heat sink 14. A layer 16 of a thermally conductive paste made in accordance with the present invention is disposed as an interface material between and in contact with the heat source 12 and the heat sink 14. While the layer 16 of thermally conductive paste can be formed in a variety of shapes and sizes to fill particular needs, it is preferred in this context that it substantially cover the entire surfaces of the heat source/heat sink interface.

[0040] As illustrated, the heat source 12 is mounted to a circuit board 18. The heat source 12 is operably connected to an electrical source (not shown) and operates conventionally. As heat is generated by the heat source 12, the heat is conducted from a heat source outer surface 13 across the layer of thermally  
5 conductive paste of the present invention to a heat sink inner surface 15. The heat is thereafter conventionally dissipated to the atmosphere through the heat sink 14, as known in the art. Additionally, because the layer 16 of thermally conductive paste substantially covers both the heat source outer surface 13 and the heat sink inner surface 15, thermal contact resistance is minimized.

10 [0041] Accordingly, the present invention is also directed to an electronic apparatus that includes a heat source, a heat sink, and a layer of a thermally conductive paste of the present invention disposed between and in contact with the heat source and the heat sink.

[0042] The present invention is yet further directed to a method of  
15 removing heat from a heat source which involves providing a heat sink proximate the heat source and disposing a layer of a thermally conductive paste of the present invention between and in contact with the heat source and the heat sink. The method is useful, for example, in aiding in the dissipation of heat from a microelectronic device or apparatus.

20 [0043] The examples that follow are focused on the addition of various thermally conductive fillers to organic vehicles for the purpose of providing a thermal paste which is conformable, spreadable and relatively high in thermal conductivity. The fillers evaluated here are carbons (such as, carbon black, 1  $\mu\text{m}$  and 5  $\mu\text{m}$  graphite particles, 0.1  $\mu\text{m}$  diameter discontinuous carbon filaments and  
25 25  $\mu\text{m}$  diamond particles) and 1  $\mu\text{m}$  and 3  $\mu\text{m}$  nickel particles.

[0044] Of all these fillers, carbon black, which is porous, is the only type that is itself spreadable (compressible). Galli, *Plastics Compounding* 5:22-32 (1982), which is hereby incorporated by reference in its entirety. The spreadability is believed to be the reason behind the superior performance of  
30 carbon black compared to all the other fillers investigated. Helsen et al., *Colloid. & Polym. Sci.* 264:619-622 (1986); Mewis et al., *Colloids & Surfaces* 22:271-289

(1987); Genz et al., *J. Colloid & Interface Sci.* 165:212-220 (1994), which are hereby incorporated by reference in their entirety.

[0045] Furthermore, the porosity of a carbon black particle allows penetration of the vehicle into a carbon black particle, thereby enabling the resulting paste to have high fluidity, as previously shown for the case of oil as the vehicle. Ishii et al., *Carbon* 39:2384-2386 (2001); Trappe et al., *Phys. Rev. Lett.* 85:449-452 (2000); Kratochvil et al., *Colloids & Surfaces* 5:179-186 (1982); Fitzgerald et al., *Rubber Chem. & Tech.* 55:1569-1577 (1982); Amari, *Progress in Organic Coatings* 31:11-19 (1997), which are hereby incorporated by reference in their entirety.

[0046] The examples further provide a comparative study of various organic vehicles and vehicle systems, such as, PEG with 0-15 vol.% dissolved ethyl cellulose and di(ethylene glycol) butyl ether with 0-40 vol.% dissolved ethyl cellulose. The comparative evaluation pertains both to the effectiveness of the thermal paste and the temperature resistance, as both attributes are relevant to the thermal paste application.

## **EXAMPLES**

### **Example 1 - Preparation of Paste Formulations**

[0047] The polyethylene glycol,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{11}\text{H}$ , ("PEG") used as an organic vehicle was PEG 400 (EM Science, Gibbstown, NJ). It had a molecular weight of 400 amu. It was a liquid at room temperature and optionally contained ethyl cellulose (Sigma Chemical Co., St. Louis, MO) at either 3 or 5 vol.%. The ethyl cellulose was a white powder that was dissolved in the vehicle. It served to improve the dispersion and suspension of the solids in the pastes.

[0048] The other organic vehicle used was di(ethylene glycol) butyl ether (Aldrich Chemical Co., Inc., Milwaukee, WI). It optionally contained ethyl cellulose (Sigma Chemical Co., St. Louis, MO) at 10, 20, 30 or 40 vol.%.

[0049] The carbon black used was a type for electrical conductivity and easy dispersion (Vulcan XC72R GP-3820; Cabot Corp., Billerica, MA). It consisted of porous agglomerates of carbon particles of particle size 30 nm, density 1.7 - 1.9 g/cm<sup>3</sup>, nitrogen specific surface area 254 m<sup>2</sup>/g and maximum ash

content 0.2% . The carbon black powder was mixed with a vehicle by hand, stirring to form a uniform paste.

[0050] Other thermally conductive solids, all used at 0.27 vol.% for the sake of comparison, were graphite particles (Asbury Graphite Mills, Inc., Asbury, NJ, (i) artificial graphite, Grade Ultra Fine 440, 99.4% typical carbon content, 1  
5  $\mu\text{m}$  typical size, and (ii) natural crystalline flake, Grade Micro 850, 98.5% minimum carbon content, 5  $\mu\text{m}$  typical size), carbon filaments (Applied Sciences Inc., Cedarville, OH, 0.1  $\mu\text{m}$  diameter, >100  $\mu\text{m}$  length, with intertwined morphology and fishbone texture), 1  $\mu\text{m}$  nickel particles (INCO, Inc.,  
10 Missassauga, Ontario, CA, Type 210), 3  $\mu\text{m}$  nickel particles (Novamet Specialty Products Corp., Wyckoff, NJ, Type 525, 15 to 20  $\mu\text{m}$  length), and 25  $\mu\text{m}$  diamond particles (Warren Superabrasives, Olyphant, PA, Type MB).

[0051] The pastes were prepared by first dissolving ethyl cellulose (if applicable) to the vehicle (either PEG or butyl ether). The dissolution was  
15 performed at room temperature for butyl ether, but at about 60°C (with heat provided by a hot plate) for PEG. The heating for the case of PEG was to hasten the dissolution. After this, the thermally conductive solid ingredient was added. Mixing was conducted by using a ball mill and stainless steel balls. After mixing, the paste was placed in a vacuum chamber (which involved a mechanical vacuum  
20 pump) for the purpose of air bubble removal.

#### **Example 2 - Thermal Contact Conductance Measurement**

[0052] As generally depicted in Figure 2, a layer of a thermally conductive paste 16 (or solder) was sandwiched between the flat surfaces of two copper disks  
20,22 (both surfaces of each disk having been mechanically polished by using  
25 0.05  $\mu\text{m}$  alumina particles), which had diameter 12.6 mm and thickness of 1.16 mm for one disk and 1.10 mm for the other disk. The thermal contact conductance between two copper disks with and without a layer of thermally conductive paste 16 (or solder) was measured using the transient laser flash method. Xu et al., *J. Electron. Pkg.* 124:188-191 (2002); Xu et al., *J. Electron.*  
30 *Pkg.* 122:128-131 (2000); Parker et al., *J. Appl. Phys.* 32:1679-1683 (1961); Inoue et al., *Yosetsu Gakkai Ronbunshu / Quarterly J. Jap. Welding Soc.*, 6:130-134 (1988), which are hereby incorporated by reference in their entirety.

[0053] The pressure on the sandwich was controlled at 0.46, 0.69 and 0.92 MPa (depicted in Figure 2 as arrow A). This is because the pressure affects the thermal contact conductance, even for a material that is not resilient. Xu et al., *J. Electron. Pkg.* 122:128-131 (2000), which is hereby incorporated by reference in its entirety. The thickness of the thermally conductive paste was 25  $\mu\text{m}$  or less. The uniform distribution of the paste in the plane of the sandwich was made possible by the fluidity of the paste and the use of pressure. The thermally conductive paste thickness was obtained by subtracting the thicknesses of the two copper disks from the thickness of the sandwich, such that all thicknesses were measured using a micrometer. The thermally conductive paste thickness for all cases was the same before and after the conductance measurement.

[0054] For the sake of comparison, solder (applied in the molten state) was also used as a thermal interface material (i.e., substituted for the layer of thermally conductive paste 16). The solder was tin-lead-antimony (63 Sn-36.65 Pb-0.35 Sb), with activated Rosin flux core (Solder Type 361A-20R by Measurements Group, Inc., Raleigh, NC). Molten solder at a temperature of 187°C, as measured by using a Type-T thermocouple, was sandwiched between copper disks that had been preheated to this temperature also. This temperature was above the liquidus temperature of 183°C. The heat was provided by a hot plate. The copper-solder-copper sandwich was allowed to cool on the hot plate with the power off under slight pressure. The thickness of the solder was 25  $\mu\text{m}$  or less.

[0055] The finite element program ABAQUS® (Abaqus, Inc., Pawtucket, RI) was used to calculate the thermal contact conductance through temperature vs. time curves, which were experimentally obtained. Xu et al., *J. Electron. Pkg.* 122:128-131 (2000), which is hereby incorporated by reference in its entirety. The calculation assumed no thickness and no heat capacity for the interface between the two copper disks. In addition, it assumed no heat transfer between specimen and environment except for the absorption of laser energy by the specimen. Moreover, it assumed that the laser energy was uniformly absorbed on the surface of the specimen, that the heat flow was one-dimensional, and that the thermal contact conductance between the two copper disks was uniform. The

validity of these assumptions is supported by the calibration result and error analysis given below.

[0056] Referring again to Figure 2, a Coherent General Everpulse Model 11 Nd glass laser (Coherent, Inc., Santa Clara CA) (depicted generally in Figure 2 as 24) with a pulse duration of 0.4 ms, a wavelength of 1.06  $\mu\text{m}$  and a pulse energy up to 15 J was used for impulse heating. The laser power was adjusted to allow the temperature rise of the specimen to be between 0.5 and 1.0°C. The upper surface of disk #1, 20, on which the laser beam (depicted as arrow B) would directly hit had been coated by carbon in order to increase the extent of laser energy absorption relative to the extent of reflection. A first E-type thermocouple (not shown) was attached to the back surface of disk #2, 22, for monitoring the temperature rise. A second thermocouple of the same type (not shown) was put ~30 cm above the specimen holder to detect the initial time that the laser beam (arrow B) came out.

[0057] A National Instruments DAQPad-MIO16XE-50 data acquisition board (National Instruments, Austin, TX) with a data acquisition rate up to 20,000 data points per second at 16 bites resolution, along with NI-DAQ interface software coded in Visual Basic® (Microsoft® Corp., Redmond, WA) was used to monitor the response of both thermocouples simultaneously. A plexiglass sample holder 26, bolt 28 and rubber insulator 30, were used to facilitate pressure application. A Sensotec Model 13 (Columbus, OH) load cell 32 was used for pressure measurement. Calibration using a standard graphite specimen was performed before testing each specimen in order to ensure measurement accuracy. The data acquisition rate used for each test was adjusted so that there were at least 100 temperature data points during the temperature rise.

[0058] The experimental error in transient thermal contact conductance measurement consists of random error due to experimental data scatter, and systematic error mainly due to the lag of the thermocouple response and partly due to the method used to calculate the conductance from the temperature data. The higher the thermal contact conductance, the greater is the error. The thermal diffusivity of a standard NBS 8426 graphite disk (thickness = 2.62 mm), which had a similar transient temperature rise time as the copper sandwich with the

highest thermal contact conductance, was measured prior to testing each specimen in order to determine the systematic error, if any. The random error shown by the  $\pm$  value was determined by measurement of five specimens.

**Example 3 - Viscosity Testing**

- 5    [0059]        The viscosity of the formulations was measured by using a viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA, Model LVT Dial-Reading Viscometer, with Model SSA-18/13R Small Sample Adaptor).

**Example 4 - Thermal Stability Testing**

- 10    [0060]        The thermal stability of the formulations was tested by thermogravimetry, as conducted by heating in air from room temperature to 150°C at a rate of 2°C/min. A Perkin Elmer(Newark, CT) TGA7 instrument was used.

**Example 5 - Evaluation of Thermal Contact Conductance**

- 15    [0061]        Table 1 gives thermal contact conductance for various thermal pastes (containing 0 to 3.20 vol.% carbon black) between copper disks at various contact pressures. The paste was below 25  $\mu$ m in thickness. As seen in Table 1, without carbon black, the optimum ethyl cellulose content for attaining high thermal contact conductance using PEG as the vehicle base was 5 vol.%. The conductance was less when the ethyl cellulose content was below or above this value. This is attributed to the increase in both conductivity and viscosity
- 20    provided by the ethyl cellulose. The conductivity helped the contact conductance, thus causing the conductance to increase as the cellulose content increased from 0 to 5 vol. %. On the other hand, the viscosity was detrimental to the contact conductance, thus causing the conductance to decrease as the cellulose content increased from 5 to 15 vol.%.
- 25    [0062]        The addition of carbon black to PEG containing 3 vol.% ethyl cellulose increased the contact conductance, provided that the carbon black content was 1.25 vol.% or below (Table 1). Exceeding this content caused the contact conductance to drop, as shown for a carbon black content of 1.5 vol.%, which gave even lower conductance than the case without carbon black. In the
- 30    case of PEG containing 5 vol.% ethyl cellulose, the conductance was diminished greatly by the carbon black addition (even just 0.5 vol.% carbon black). This is attributed to the resulting high viscosity when ethyl cellulose was present at 5



vol.% and the further increase in viscosity upon the carbon black addition. The viscosity results are described in Example 6. Among the PEG based pastes, the highest contact conductance of  $30 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  was attained by using 3 vol.% ethyl cellulose and 1.25 vol.% carbon black.

5    **[0063]**           Referring again to Table 1, it is seen that for butyl ether without carbon black, the optimum ethyl cellulose content for attaining high contact conductance was 30 vol.% when the contact pressure was 0.46 MPa and was 20 vol.% when the pressure was 0.69 or 0.92 MPa. Due to its low viscosity, butyl ether dissolved ethyl cellulose powder more easily than did PEG. However, the  
10   conductance attained by butyl ether, whether with or without ethyl cellulose, is lower than that attained by PEG, whether with or without carbon black.

**[0064]**           The addition of carbon black to butyl ether had little effect on the contact conductance, unless the ethyl cellulose content was high (40 vol.%). In this case, the conductance increased with carbon black content from 0 to 0.20  
15   vol.% and decreased with carbon black content from 0.20 to 0.53 vol.%. The optimum carbon black content 0.20 vol.%, at which conductance reached  $28 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ .

**[0065]**           For pastes based on PEG (with 3 vol.% ethyl cellulose) and butyl ether (with 40 vol.% ethyl cellulose), the conductance was maximum at an  
20   intermediate content of carbon black. This trend had been previously reported for boron nitride particle pastes based on lithium doped PEG. Xu et al., *J. Electron. Pkg.*, 124: 188-191 (2002) , which are hereby incorporated by reference in their entirety. It is attributed to the required compromise between thermal conductivity and viscosity, both of which increase with increasing solid content. The viscosity  
25   results are described in Example 6.

**[0066]**           The highest conductance attained by PEG-based and butyl ether-based pastes is similar. However, the optimum carbon black content is much higher for the PEG-based paste and the optimum ethyl cellulose content is much lower for the PEG-based paste. Due to the importance of a low viscosity, the use  
30   of a high ethyl cellulose content requires that of a low carbon black content, and the use of a high carbon black content requires that of a low ethyl cellulose content.

Table 1

Thermal Interface Material			Conductance ( $10^4$ W/m <sup>2</sup> .°C)		
Vehicle	Vol.% EC	Vol. % CB	0.46 MPa	0.69 MPa	0.92 MPa
PEG	0	0	11.00 ± 0.30	-	-
PEG	3	0	12.02 ± 0.86	13.98 ± 1.06	15.57 ± 1.03
PEG	5	0	18.51 ± 0.83	18.92 ± 0.91	20.74 ± 1.52
PEG	7.5	0	17.61 ± 0.11	17.60 ± 0.75	19.21 ± 0.79
PEG	10	0	12.31 ± 0.52	12.29 ± 0.61	14.69 ± 0.80
PEG	15	0	4.14 ± 0.25	4.41 ± 0.07	4.59 ± 0.33
PEG	3	0	12.02 ± 0.86	13.98 ± 1.06	15.57 ± 1.03
PEG	3	0.50	15.45 ± 0.94	17.67 ± 1.09	19.10 ± 0.43
PEG	3	1.00	18.83 ± 1.08	19.41 ± 1.38	22.81 ± 1.12
PEG	3	1.25	29.90 ± 0.79	28.98 ± 2.11	29.63 ± 1.92
PEG	3	1.50	9.92 ± 0.57	11.50 ± 0.90	12.29 ± 1.06
PEG	5	0	18.51 ± 0.83	18.92 ± 0.91	20.74 ± 1.52
PEG	5	0.50	9.00 ± 0.14	13.16 ± 0.19	13.28 ± 0.07
PEG	5	0.75	11.71 ± 0.44	12.90 ± 0.31	14.83 ± 0.63
PEG	5	1.00	10.61 ± 0.20	11.45 ± 0.33	11.61 ± 0.50
BE	0	0	2.89 ± 0.10	-	3.86 ± 0.08
BE	10	0	3.65 ± 0.13	4.55 ± 0.21	5.68 ± 0.06
BE	20	0	3.70 ± 0.08	5.11 ± 0.05	6.40 ± 0.11
BE	30	0	4.60 ± 0.28	5.08 ± 0.15	5.54 ± 0.21
BE	40	0	3.67 ± 0.13	4.37 ± 0.12	4.61 ± 0.06
BE	0	0	2.89 ± 0.10	-	3.86 ± 0.08
BE	0	1.34	2.14 ± 0.08	-	3.75 ± 0.06
BE	0	2.14	2.85 ± 0.04	-	3.08 ± 0.08
BE	0	2.67	1.64 ± 0.10	-	2.37 ± 0.0+
BE	0	3.20	1.62 ± 0.07	-	2.32 ± 0.06
BE	10	0	3.65 ± 0.13	4.55 ± 0.21	5.68 ± 0.06
BE	10	0.53	1.10 ± 0.06	2.99 ± 0.06	4.42 ± 0.06
BE	10	1.34	4.53 ± 0.15	5.35 ± 0.19	5.43 ± 0.31
BE	10	2.14	3.75 ± 0.11	4.64 ± 0.22	4.75 ± 0.17
BE	10	2.67	1.75 ± 0.05	2.75 ± 0.06	4.05 ± 0.18
BE	20	0	3.70 ± 0.08	5.11 ± 0.05	6.40 ± 0.01
BE	20	0.53	4.02 ± 0.13	5.17 ± 0.09	5.47 ± 0.28
BE	20	1.34	4.13 ± 0.13	5.25 ± 0.16	5.52 ± 0.11
BE	20	2.14	5.00 ± 0.17	5.39 ± 0.13	5.64 ± 0.20
BE	20	2.67	1.08 ± 0.07	1.13 ± 0.03	1.45 ± 0.03
BE	30	0	4.60 ± 0.28	5.08 ± 0.15	5.54 ± 0.21
BE	30	0.27	3.41 ± 0.14	3.94 ± 0.10	4.17 ± 0.05
BE	30	0.53	4.23 ± 0.16	5.60 ± 0.22	6.62 ± 0.32
BE	30	1.07	1.65 ± 0.02	2.13 ± 0.05	2.88 ± 0.07
BE	40	0	3.67 ± 0.13	4.37 ± 0.12	4.61 ± 0.06
BE	40	0.10	10.90 ± 1.10	16.19 ± 1.02	16.93 ± 0.12
BE	40	0.20	27.43 ± 2.75	28.41 ± 2.12	28.03 ± 1.57
BE	40	0.27	18.94 ± 0.60	24.87 ± 1.00	25.74 ± 1.20
BE	40	0.30	13.62 ± 1.32	17.05 ± 1.26	18.54 ± 1.53
BE	40	0.40	6.02 ± 0.58	7.68 ± 0.10	9.56 ± 0.62
BE	40	0.53	4.95 ± 0.15	5.58 ± 0.17	5.55 ± 0.11
EC = ethyl cellulose CB = carbon black PEG = polyethylene glycol BE = di(ethylene glycol) butyl ether					

[0067] Table 2 gives thermal contact conductance for thermal pastes in the form of di(ethylene glycol) butyl ether containing 40 vol.% ethyl cellulose and 0.27 vol.% thermally conductive solids, as tested between copper disks at various contact pressures. The paste was below 25  $\mu\text{m}$  in thickness.

5 [0068] Table 2 shows that carbon black is a much more effective conductive additive than graphite, nickel and diamond particles and carbon filaments, for it provides a thermal paste that gives an exceptionally high thermal contact conductance. The superiority of carbon black occurs in spite of the relatively poor thermal conductivity of carbon black. It is attributed to the  
10 conformability and spreadability of the paste, as enhanced by the compressibility of the carbon black agglomerates.

[0069] The compressibility of carbon black and the consequent electrical connectivity attained upon squeezing, have been previously reported. In particular, as an electrically conductive additive to a non-conductive  $\text{MnO}_2$  particle  
15 cathode of an electrochemical cell, carbon black resulted in a lower resistivity than carbon filament without graphitization (same as the carbon filament used in this work), due to the squeezing of the carbon black between adjacent  $\text{MnO}_2$  particles. Frysz et al., *J. Power Sources* 58:41-54 (1996); Lu et al., *Carbon* 40:447-449 (2000), which are hereby incorporated by reference in their entirety.  
20 In contrast, the other conductive solids investigated are not compressible. Carbon black is even superior to single-walled carbon nanotubes, pastes of which were tested using the methods and equipment described here. Xu et al., *J. Electron. Mater.* (2004), which is hereby incorporated by reference in its entirety. For comparison, these results are shown in Table 2. Conformability and spreadability  
25 are more important than thermal conductivity in governing thermal paste performance.

[0070] The use of solder in place of a thermal paste gave a thermal contact conductance of  $(20.08 \pm 0.60) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  (not shown in Tables). This value is consistent with that previously reported in the literature for the same testing  
30 method and configuration. Xu et al., *J. Electron. Pkg.* 124: 188-191 (2002), which is hereby incorporated by reference in its entirety. Thus, the optimized

carbon black pastes of the present invention are significantly superior to solder as thermally conductive interface materials.

[0071] The limited effectiveness of solder occurs in spite of the high thermal conductivity of solder. This is partly due to the reaction between solder and the copper disks. This reaction results in copper-tin intermetallic compounds at the solder-copper interface. Grivas et al., *J. Electron Mater.* 15:355-359 (1986); Tu, *Mater. Chem. Phys.* 46:217-223 (1996); Tsutsumi et al., *Int. J. Hybrid Microelec.* 7:38-43 (1984), which are hereby incorporated by reference in their entirety. The compound formation causes the solder to not wet the copper surface. Kim et al., *Mat. Res. Soc.* 183-188 (1995), which is hereby incorporated by reference in its entirety. This leads to increased difficulty of the solder to conform to the surface topography of the copper. Conformability and spreadability are more important than thermal conductivity in governing the performance of a thermal interface material.

[0072] The thermal contact conductance values reported herein for the paste formulations (Tables 1 and 2) and solder as thermal interface materials were all obtained using the same specimen configuration, testing method and data analysis algorithm, and the values are reliable on a relative scale. However, the values deviate from the true values, due to the fact that the data analysis algorithm neglects the thickness of the thermal interface material. Luo et al., *Int. J. Microcircuits Electron. Pkg.* 24:141-147 (2001), which is hereby incorporated by reference in its entirety.

**Table 2**

THERMALLY CONDUCTIVE SOLID	CONDUCTANCE ( $10^4$ W/m <sup>2</sup> .°C)		
	0.46 MPa	0.69 MPa	0.92 MPa
Carbon Black	18.94 ± 0.60	24.87 ± 1.00	25.74 ± 1.20
Graphite (5 µm)	3.03 ± 0.09	3.67 ± 0.08	4.02 ± 0.12
Graphite (1 µm)	1.52 ± 0.03	1.77 ± 0.04	2.04 ± 0.05
Nickel (3 µm)	1.85 ± 0.05	2.14 ± 0.02	2.84 ± 0.04
Nickel (1 µm)	0.91 ± 0.07	2.03 ± 0.10	2.66 ± 0.03
Diamond (25 µm)	1.15 ± 0.02	1.21 ± 0.09	1.54 ± 0.03
Carbon Filaments (0.1 µm diameter)	1.09 ± 0.03	1.32 ± 0.02	1.51 ± 0.03
Single-walled carbon nanotubes	13.5 ± 0.2	13.8 ± 0.3	14.1 ± 0.4

**Example 6 - Evaluation of Viscosity**

[0073] Table 3 shows the viscosity of selected pastes, as measured at various appropriate shear rates. The addition of ethyl cellulose to either PEG or butyl ether monotonically increased the viscosity, as shown in the absence of  
5 carbon black. PEG alone was higher in viscosity than butyl ether alone. However, PEG with the optimum ethyl cellulose content of 3 vol.% was much lower in viscosity than butyl ether with the optimum ethyl cellulose content of 40 vol.%. The addition of carbon black monotonically increased the viscosity, as shown for PEG containing 3 vol.% ethyl cellulose and for butyl ether containing  
10 40 vol.% ethyl cellulose.

[0074] The PEG with 5 vol.% ethyl cellulose and the PEG-based paste containing 3 vol.% ethyl cellulose and 1.25 vol.% carbon black were similar in viscosity. The latter gave a higher contact conductance than the former, due to a decrease in the ethyl cellulose content and an increase in the carbon black content.  
15 Thus, adjustment of the contents of both ethyl cellulose and carbon black is needed in order to attain an optimized thermal paste formulation.

[0075] As shown in Table 1, the butyl ether-based paste with 40 vol.% ethyl cellulose and 0.20 vol.% carbon black and the PEG-based paste with 3 vol.% ethyl cellulose and 1.25 vol.% carbon black are the two thermal pastes of the  
20 present invention that gave the highest thermal contact conductance. As shown in Table 3, although the two pastes gave similarly high values of the contact conductance, the butyl ether-based paste exhibited a much higher viscosity than the PEG-based paste.

[0076] Table 3 also shows that the viscosity of the butyl ether-based paste  
25 with 40 vol.% ethyl cellulose was lower when the paste contained 0.20 vol.% graphite particles (1 or 5  $\mu\text{m}$ ) or carbon filaments than when it contained 0.20 vol.% carbon black. However, it was noticed during paste mixing that the carbon black paste was much smoother than the graphite particle paste. The smoothness of the paste is apparently more important than the viscosity in governing thermal  
30 paste performance. Perhaps smoothness relates more closely to the conformability than a low viscosity.

[0077] Referring again to Table 3, the viscosity of butyl ether-based paste with 40 vol.% ethyl cellulose and 0.20 vol.% solid increased in the order: 1  $\mu\text{m}$  graphite particles, 5  $\mu\text{m}$  graphite particles and carbon filaments. This trend is consistent with the notion that a larger particle size tends to result in a paste with a higher viscosity and that filaments tend to result in a higher viscosity than particles.

**Table 3**

Vehicle	Vol.% EC	Vol.% CB	Viscosity (cP)							
			0.79 (s <sup>-1</sup> )	2.0 (s <sup>-1</sup> )	2.6 (s <sup>-1</sup> )	4.0 (s <sup>-1</sup> )	6.6 (s <sup>-1</sup> )	7.9 (s <sup>-1</sup> )	16 (s <sup>-1</sup> )	40 (s <sup>-1</sup> )
PEG	0	0	-	-	-	125	-	120	120	-
PEG	3.0	0	-	-	-	160	-	145	140	-
PEG	5.0	0	-	-	-	190	-	190	195	-
PEG	7.5	0	-	-	-	240	-	250	-	-
PEG	3.0	0.50	-	-	-	175	-	185	185	-
PEG	3.0	1.25	-	-	-	200	-	195	200	-
PEG	3.0	1.50	-	-	-	210	-	210	215	-
BE	0	0	-	-	-	-	-	-	-	<10
BE	10	0	-	-	-	-	-	-	25	20
BE	30	0	580	520	-	540	-	-	-	-
BE	40	0	-	-	4,000	-	3,900	-	-	-
BE	40	0.10	-	-	4,720	-	4,400	-	-	-
BE	40	0.20	-	-	5,200	-	4,800	-	-	-
BE	40	0.30	-	-	5,600	-	5,200	-	-	-
BE	40	0.20 <sup>a</sup>	-	-	4,000	-	3,900	-	-	-
BE	40	0.20 <sup>b</sup>	-	-	4,800	-	4,480	-	-	-
BE	40	0.20 <sup>c</sup>	-	-	5,000	-	4,720	-	-	-
EC = ethyl cellulose CB = carbon black BE = di(ethylene glycol) butyl ether			<sup>a</sup> Graphite particles (1 $\mu\text{m}$ ) <sup>b</sup> Graphite particles (5 $\mu\text{m}$ ) <sup>c</sup> Carbon filaments							

[0078] Although the viscosity is a useful suggestive indicator of thermal paste performance, it is not the same as the conformability, which is the attribute that really governs thermal paste performance. Since there is no standardized method of conformability measurement, this work resorted to viscosity measurement.

#### **Example 7 - Evaluation of Thermal Stability**

[0079] Figures 3 and 4 respectively, show the thermogravimetric results for PEG and butyl ether (with and without ethyl cellulose in each case, but

without carbon black, which does not affect the thermal stability of the dispersion). Without ethyl cellulose, PEG is much more stable thermally than butyl ether. The dissolution of ethyl cellulose diminished the thermal stability of PEG, but increased that of butyl ether.

- 5 [0080] Table 4 shows a comparison of thermogravimetric results of these thermal pastes at three temperatures. At 50°C and 75°C, butyl ether containing ethyl cellulose is more stable thermally than PEG containing ethyl cellulose, but at 100°C, the reverse is true. Above about 100°C, the weight loss of butyl ether, whether with or without ethyl cellulose, is extensive (more than 50% weight loss at 150°C). However, the weight loss remains less than 9% even at 150°C for PEG, whether with or without ethyl cellulose. Therefore, butyl ether-based pastes are not suitable for use above 100°C, whereas PEG-based pastes are suitable for use up to at least 150°C.

**Table 4**

Thermal Interface Material		Residual Weight (%)		
Vehicle	Vol.% EC	50°C	75°C	100°C
PEG	0	99.81	99.22	98.91
PEG	3	98.73	95.47	93.36
BE	0	98.98	96.11	84.67
BE	40	99.33	97.26	89.68
EC = ethyl cellulose PEG = polyethylene glycol BE = di(ethylene glycol) butyl ether				

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- [0081] The use of a PEG-based paste (containing 3 vol.% dissolved ethyl cellulose and dispersed carbon black in the optimum amount of 1.25 vol.%) as a thermal interface material between copper disks results in a thermal contact conductance of  $30 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ , compared to a value of  $20 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  for tin/lead eutectic solder applied in the molten state. Almost as effective as the PEG-based paste is a butyl ether-based paste (containing 40 vol.% dissolved ethyl cellulose and dispersed carbon black in the optimum amount of 0.20 vol.%), which gives a thermal contact conductance of  $28 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ . The PEG-based paste is superior to the butyl ether-based paste in the thermal stability at 100°C and above, though the reverse is true at 75°C and below. The superiority of the

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formulations of the present invention to solder as thermal interface materials may presumably be due to the reaction between solder and copper and the consequent poor conformability of molten solder with copper.

5     **[0082]**         The use of PEG by itself gives a thermal contact conductance of  $11 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ . The dissolution of ethyl cellulose at an optimum concentration of 5 vol.% increases the conductance to  $19 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ . The use of butyl ether by itself gives a contact conductance of  $3 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ . The dissolution of ethyl cellulose at the optimum concentration of 20 to 30 vol.% gives a conductance ranging from  $4 \times 10^4$  to  $6 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ .

10   **[0083]**         The addition of carbon black to PEG helps the conductance when the ethyl cellulose is at 3 vol.% and the carbon black content is at 1.25 vol.% or below. The addition of carbon black to PEG degrades the conductance when the ethyl cellulose is at 3 vol.% and carbon black is at 1.5 vol.%, or when the ethyl cellulose is at 5 vol.%. These effects are presumably due to the importance of  
15   conformability and spreadability to the thermal paste performance. Both carbon black and ethyl cellulose cause the viscosity of the paste to increase, so excessive amounts of these ingredients degrade the conductance.

20   **[0084]**         The optimum carbon black content is higher for PEG than butyl ether based, whereas the optimum ethyl cellulose content is higher for butyl ether than PEG. In spite of the difference in carbon black content, the thermal contact conductance is similar between the optimized PEG-based paste and the optimized butyl ether-based paste. Since carbon black is the ingredient in the paste that is most conductive thermally, this implies that the conformability and spreadability are more important than the thermal conductivity in governing thermal paste  
25   performance.

30   **[0085]**         Moreover, in spite of its own relatively low thermal conductivity, carbon black is much more effective than graphite, nickel and diamond particles and carbon filaments, all evaluated at the same volume fraction, for providing thermal pastes. This is attributed to the compressibility of a carbon black agglomerate and the consequent conformability and spreadability of the paste.



**[0086]** Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various additions, substitutions, modifications and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the  
5 scope of the invention as defined in the claims which follow.